

# Ag(I) Catalysed Oxidation of Congo Red by Potassium Peroxydisulphate : A Kinetic Approach



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## Abstract

Kinetic investigation of Ag (I) catalysed oxidation of an azo dye. Congo red in presence of sulphuric acid has been made. The reaction shows first order Kinetics both in  $[S_2O_8^{2-}]$  and zero order in [congo red] variation in  $[H_2SO_4]$  has no significant effect on the rate of oxidation. Increase of ionic strength in the medium decreases the rate constant. A 1:1 stoichiometry was observed and the reaction mixture initiates vinyl polymerisation various thermodynamic parameters have been computed and recorded. A suitable mechanism to account for the obtained kinetic results have been proposed.

**Keywords:** Oxidation, Kinetics, Mechanism, Peroxydisulphate, Order of reaction, Congo Red.

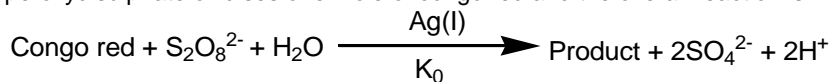
## Introduction

Potassium peroxydisulphate has been used as an oxidant for the oxidation of a number of organic and inorganic substances<sup>1, 2</sup>. The catalytic reduction of peroxydisulphate with different organic compounds has been used to determine the micro amounts of silver, iron and vanadium<sup>3</sup>. New reactions involving the oxidation of ethylenediaminetetraaceto – cobalt (II)<sup>4</sup> and fluorescein<sup>5</sup> substrates with peroxydisulphate catalysed by Ag(I) have been investigated. In this paper, we report the mechanism of the silver (I) ion catalysed oxidation of congo red by  $S_2O_8^{2-}$ .

Stock solutions of congo red and silver (I) were prepared by dissolving their requisite quantity in redistilled water. The working solution were prepared by the process of dilution. Standard solution of  $K_2S_2O_8$  was prepared afresh just before use by dissolving the required quantity in redistilled water to avoid any decomposition. All other reagents were of analytical grade.

The solution of  $S_2O_8^{2-}$ , sodium perchlorate, congo red and  $H_2SO_4$  were each thermostated at the desired temperature. The reaction was started by adding the required quantity of silver (I) solution to a thermally equilibrated solution of the reaction vessel. The course of the reaction was followed by measuring the time dependence of the optical density of the solution using systronic double cell colorimeter with green filter.

The reaction was studied under the conditions,  $[S_2O_8^{2-}] \gg [congo\ red]$  throughout the investigation. After completion of the reaction, the amount of the congo red consumed was estimated from the decrease in the optical density. It was observed that one mole of potassium peroxydisulphate oxidises one mole of congo red and the overall reaction is



The stoichiometry indicates the formation of azoxy compound as the oxidation product. This was identified by spot test<sup>6</sup>.

## Results and Discussion

The rate of oxidation of congo red by peroxydisulphate in the absence of Ag(I) ion was very slow. However, it was found that the silver(I) ions catalyse the oxidation of congo red by  $S_2O_8^{2-}$ .

### Dependence of Rate of Oxidation on the External Variables Concentration of potassium peroxydisulphate

The reaction was studied at several initial concentrations of peroxydisulphate. As is shown in table 1, the plot of  $k_0$  versus  $[S_2O_8^{2-}]$  is a straight line passing through the origin. The fairly constant values of

$k_1 = k_0/[S_2O_8^{2-}]$  for different concentrations of peroxydisulphate further indicate a first order dependence in  $[S_2O_8^{2-}]$

Table-1

Effect of varying  $[S_2O_8^{2-}]$  on the reaction rate :  $[congo\ red] = 3.3 \times 10^{-5}\ M$ ,  $[Ag(I)] = 8.3 \times 10^{-4}\ M$ ,  $[H_2SO_4] = 1.0\ M$ ,  $[NaClO_4] = 0.33\ M$ , Temp. = 303 K

$[S_2O_8^{2-}] \times 10^6/M$	0.60	1.60	3.30	5.00	6.60	8.30
$10^7 k_0/M^{-1} \min^{-1}$	1.75	2.50	4.50	7.25	9.50	12.00
$k_0/[S_2O_8^{2-}] = 10^3 k_1/\min^{-1}$	2.90	1.56	1.44	1.45	1.44	1.44

#### Concentration of Congo Red

Kinetic runs were carried out keeping the concentration of  $S_2O_8^{2-}$  in excess over that of substrate. The dependence of the reaction rate on [congo red] has been studied by varying the concentration of substrate in the range of (1.60-5.83)

$\times 10^{-5}\ M$  at a constant concentration of other reactants (Table 2). A plot of absorbance versus time is a straight line. The pseudo zero order rate constant,  $k_0$  in congo red were evaluated from the slopes of these linear plots. This indicates that the rate of oxidation was independent of [substrate].

Table-2

Effect of varying [congo red] on the reaction rate :  $[S_2O_8^{2-}] = 3.3 \times 10^{-4}\ M$ ,  $[Ag(I)] = 8.3 \times 10^{-4}\ M$ ,  $[H_2SO_4] = 1.0\ M$ ,  $[NaClO_4] = 0.33\ M$ , Temp. = 303 K

[congo red] $\times 10^5 /M$	1.60	2.50	3.30	4.17	5.00	5.83
$k_0 \times 10^7/M^{-1} \min^{-1}$	4.60	4.50	4.75	4.40	4.60	4.20

#### Catalyst concentration

Acceleration in the rate with the increase in  $[Ag(I)]$  is evident from the rate data in Table 3. The plot of  $K_0$  vs  $[Ag(I)]$  was found to be a straight line

passing through the origin. This shows the order in [catalyst] is unity which is substantiated by the constancy of first order rate constant,  $K_0'$  at different  $[Ag(I)]$ .

Table-3

Effect of varying  $[Ag(I)]$  on the reaction rate :  $[S_2O_8^{2-}] = 3.3 \times 10^{-4}\ M$ , [congo red] =  $3.3 \times 10^{-5}\ M$ ,  $[H_2SO_4] = 1.0\ M$ ,  $[NaClO_4] = 0.33\ M$ , Temp. = 303 K

$[Ag(I)] \times 10^5/M$	0.33	0.83	1.16	1.66	2.50	3.30
$K_0 \times 10^7/M^{-1} \min^{-1}$	2.00	4.75	6.75	11.25	14.75	19.00
$K_0/[Ag(I)] = 10^4 K'/\min^{-1}$	6.06	5.72	5.82	6.77	5.90	5.75

#### Acid concentration

The kinetics of the reaction was investigated at different concentrations of  $[H_2SO_4]$  in the range of (0.2 – 2.5 M). This shows that the presence of acid in the reaction media has hardly any influence on the rate of reaction.

The rate of oxidation was studied at different concentration of the added neutral salt,  $NaClO_4$ . It was observed that the reaction rate decreases with an increase in  $[NaClO_4]$ . A plot of  $\log K_0$  vs  $\sqrt{\mu}$  gave a straight line with a negative slope (Table 4).

#### Ionic strength

Table-4

Effect of varying  $[NaClO_4]$  on the reaction rate :  $[S_2O_8^{2-}] = 3.3 \times 10^{-4}\ M$ , [congo red] =  $3.3 \times 10^{-5}\ M$ ,  $[Ag(I)] = 8.3 \times 10^{-4}\ M$ ,  $[H_2SO_4] = 1.0\ M$ , Temp. = 303 K

$[NaClO_4] \times 10^4/M$	0.66	1.33	2.00	2.66	3.30	5.00
$\sqrt{\mu}\ M$	1.75	1.77	1.79	1.81	1.83	1.87
$K_0 \times 10^7 /M^{-1} \min^{-1}$	16.25	12.25	7.25	5.50	4.25	2.50

#### Radical Scavenger

To ascertain the free radical nature of the intermediate formed, the effect of radical scavenger, acrylonitrile was investigated on the studied reaction. 5 ml of 6% acrylonitrile was added to the reaction mixture it turned that reaction mixture turbid. This clearly indicates that the reaction initiates the vinyl polymerisation and oxidation proceeds through a free radical chain mechanism.

#### Effect of Temperature

The rate of oxidation of congo red by  $S_2O_8^{2-}$  was studied at different temperature (293-308 K) and the values of the various activation parameters, viz.  $E_a$ ,  $\Delta H^\ddagger$ ,  $\Delta G^\ddagger$  and  $\Delta S^\ddagger$  were calculated from the Arrhenius plot using regression analysis as :  $E_a = 52.65 \pm 1.5\ kJ\ mol^{-1}$ ,  $\Delta H^\ddagger = 50.15 \pm 2\ kJ\ mol^{-1}$ ,  $\Delta S^\ddagger = -200.4 \pm 6\ JK^{-1}\ mol^{-1}$ , and  $\Delta G^\ddagger = 110.4 \pm 1.7\ kJ\ mol^{-1}$

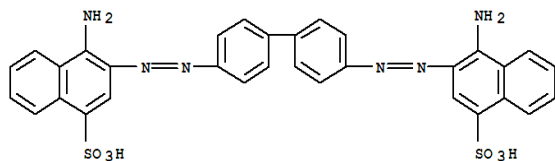
The experimentally observed kinetic law for this reaction is represented as

$$-\frac{d}{dt} [S_2O_8^{2-}] = K [Ag(I)][S_2O_8^{2-}]$$

representing that the velocity at any instant is proportional to the peroxydisulphate ion and silver (I) ion concentration.

The determined zero order with respect to congo red confirms the assumption that in the catalytic process the reaction between  $S_2O_8^{2-}$  and  $Ag(I)$  ions is the rate determining step. The negative salt effect also indicates that the rate determining step is between oppositely charged bivalent and univalent ions ( $S_2O_8^{2-}$  and  $Ag(I)$ ). The peroxydisulphate oxidation in the presence of silver ions very often occurs with negative salt effect and zero order in substrate<sup>7-10</sup>. The inhibition of rate by acrylonitrile provides the evidence that the reaction proceeds by free radical chain mechanism.

The congo red molecule contains azo group :

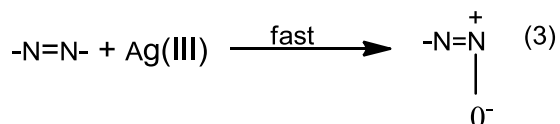
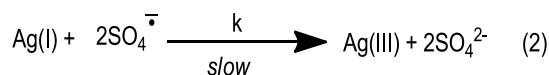
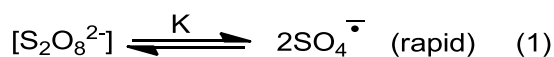


• 2 Na

### Congo Red

It has been reported that the site of the attack in azo compounds is  $-N=N-$  group<sup>11</sup>. The azo compounds are oxidised to azoxy derivatives with peroxy acids<sup>12-13</sup>

Taking into consideration the proposed mechanism for the oxidation of  $S_2O_8^{2-}$  and  $Ag(I)$  systems, and on the basis of the kinetic results obtained and products of oxidation, scheme I and II are proposed for the oxidation of congo red by  $S_2O_8^{2-}$ .



### Scheme I

$Ag(III)$  is directly involved in the two equivalent oxidation of the dye. The rate of the reaction is given by expression

$$-\frac{d}{dt} [S_2O_8^{2-}] = K [Ag(I)] [2SO_4^{\cdot -}]^2 \quad (4)$$

From the equilibrium (1), the equilibrium constant  $K$  is given by the expression

$$K = \frac{[SO_4^{\cdot -}]^2}{[S_2O_8^{2-}]} \quad (5)$$

Or

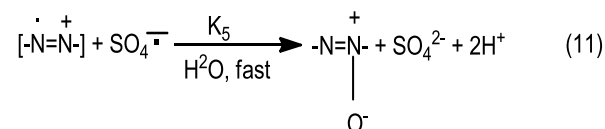
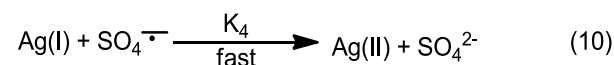
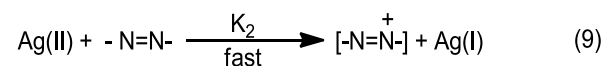
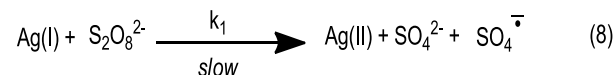
$$[SO_4^{\cdot -}]^2 = K [S_2O_8^{2-}] \quad (6)$$

Substituting this value of  $[SO_4^{\cdot -}]^2$  in the equation (4)

We obtain

$$-\frac{d}{dt} [S_2O_8^{2-}] = kK [S_2O_8^{2-}] [Ag^+] \quad (7)$$

The expression (7) is in accordance with the kinetic pattern observed. Scheme II proposes that the catalytic effect of silver ion may be explained by considering the  $Ag(I)$  and  $SO_4^{\cdot -}$  as the reaction species. The path for the oxidation of Bismark brown may also be represented by equations (8) to (12).



### Scheme II

Thus the rate of disappearance of  $[S_2O_8^{2-}]$  will be obtained by equation (12)

$$-\frac{d}{dt} [S_2O_8^{2-}] = K_1 [Ag(I)] [S_2O_8^{2-}] + K_3 [-N=N-] [S_2O_8^{2-}] \quad (12)$$

Assuming the steady state approximation with respect to  $Ag(II)$ ,  $SO_4^{\cdot -}$  and  $[-N=N]^+$  and assuming that –

$$K_1 [S_2O_8^{2-}] \ll K_4 [SO_4^{\cdot -}]$$

$$K_3 [S_2O_8^{2-}] \ll K_5 [SO_4^{\cdot -}]$$

We obtain

$$[-N=N]^+ = \frac{k_4}{k_5} [Ag(I)] \quad (13)$$

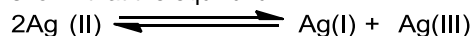
Combining equation (13) and (14), final rate expression is obtained as

$$\begin{aligned} -\frac{d}{dt} [S_2O_8^{2-}] &= K_1 [Ag(I)] [S_2O_8^{2-}] + \frac{k_3 k_4}{k_5} [Ag(I)] [S_2O_8^{2-}] \\ &= K [Ag(I)] [S_2O_8^{2-}] \quad (14) \end{aligned}$$

Where,

$$K = K_1 + \frac{k_3 k_4}{k_5}$$

The experimental rate law is in agreement with the observed kinetics. Allen and coworkers<sup>14</sup> have shown that the equilibrium



lies far to the left. Therefore participation of  $Ag(II)$  over  $Ag(III)$  is preferred. This is also in accordance with the observation of Subramaniam and Santappa<sup>15</sup>, that one electron transfer is more likely in oxidation –

reduction system between transition metal ion and ion derived from a non transition element.

#### Conclusion

Hence scheme II of the mechanism seems to be favourable.

#### Acknowledgement

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